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REMARKS

Claims 1 to 5 and 11 to 18 are in the case.

Claims 6 to 10, which were withdrawn from consideration following an election requirement, have been cancelled without prejudice. It is requested that the election requirement be reconsidered based on the submission of March 10, 2004. It is noted that there is no reference to the submission of March 10, 2004 in the Office Action.

Furthermore, it is noted that the Office Action still refers only to claims 1 to 14 (although there is a reference to claim 15 in box 6 of the Office Action Summary). As noted in the aforementioned submission of March 10, 2004, this application includes new claims 15 to 18 which were added in June 2003. These claims both depend from and thus belong with the claims elected in this application.

It is further noted that the current Office Action makes no reference to the second Information Disclosure Statement in Form PTO/SB/08A/B submitted on June 2, 2003 with the preliminary amendment presenting claims 15 to 18. On the other hand, the file history on the PAIR page for this application obtained on April 2, 2004 indicates the entry in the file of the preliminary amendment and the Information Disclosure Statement on June 3, 2003 as items 13 and 12. A copy of the PAIR page printout in pages 1 and 2 is attached for ready reference.

35 U.S.C. 112

Claims 1 to 5 and 11 to 14 are rejected under 35 U.S.C. 112, and it is indicated that applicant has not defined the terms PS<sub>UV</sub>, PS<sub>GR</sub> or PS<sub>VIS</sub> and has not indicated how they are obtained and measured.

With respect, these terms are clearly identified in the specification. Thus, page 10, in the second complete paragraph, indicates:

"Polysulphide can be measured in many ways but two of the most simple and effective are measurement by gravimetry (PS<sub>GR</sub>) and by UV or VIS absorption (PS<sub>UV</sub> or PS<sub>VIS</sub>)."

Techniques for determining concentration of polysulphide, including measurement by gravimetry and spectrophotometrically, are well established, as well as other techniques. Persons in the art to whom the specification is directed will be fully familiar with the techniques available for determination of polysulphide. The

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present invention does not reside in techniques for determining polysulphide content. For ready reference there is submitted herewith a copy of Dorris et al, Journal of Pulp and Paper Science: Vol. 20, No. 8, pgs. 211-214, "Analysis of Oxidized White Liquors. Part I: Determination of Polysulphides by Gravimetry"; and a copy of Dorris et al, Journal of Pulp and Paper Science: Vol. 20, No. 9, September 1994, pgs. 242-248, "Analysis of Oxidized White Liquors. Part II: Potentiometric Titrations for the Determination of Polysulphides and Sulphoxy Anions".

In addition, the prior art identified in the Office Action demonstrates that spectral analysis is already known in the art to determine polysulphide content. In this regard, it appears that Kester et al, Holmqvist et al, and Teder were cited for the purpose of demonstrating the use of UV spectral analysis to measure sulphide or polysulphide concentration.

With respect, the specification is fully enabling, and reconsideration is requested.

35 U.S.C. 103(a)

Claims 1 to 5 and 11 to 14 are rejected as being unpatentable over Dorris et al (U. S. Patent 5,082,526) in view of Teder (literature) and Kester et al (U. S. Patent 6,399,222) or Holmqvist et al (U. S. Patent 5,582,684) without so-called "Admitted Prior Art". The so-called Admitted Prior Art appears to be applicant's description in the experimental section of the specification in that it employed a commercial UV spectrometer to monitor polysulphide.

Background of the Invention

The present invention is based on a significant new finding of the inventors. What has been called polysulphide (PS) in previous literature sources, including the prior art referred to by the Examiner, is a mixture of **active** and **inactive** components which the inventors have named "active" and "inactive" polysulphide.

The difference between these two forms is that active polysulphide is an oxidant that can oxidize carbohydrate aldehyde groups to acids which are not susceptible to the peeling reaction during kraft pulping. The result of using active polysulphide is that pulp yield is increased. In contrast, inactive polysulphide cannot oxidize carbohydrate aldehyde groups and does **not** cause a yield increase during pulping.

Both active and inactive polysulphide are measured in the gravimetric test for polysulphide, and both are observed in UV spectrophotometric analysis except at 416 nm; at 416 nm, only active polysulphide is measured or detected. The VIS spectrometric measurement at 285 or 286 nm has contributions from both active and inactive polysulphide. The most important measurement is the concentration of active PS or the ratio of PS as measured by spectrophotometry ( $PS_{UV/VIS}$ ) to PS as measured by gravimetry ( $PS_{GR}$ ). This number describes how much of the total polysulphide is active polysulphide; the closer the ratio is to 1 the greater is the activity of the liquor.

It is fully recognized by the inventors that polysulphide can be measured spectrophotometrically, and it is not the purpose of the present invention to claim applying spectrophotometry to the measurement of polysulphide; there is a substantial body of literature on this topic including the references identified by the Examiner. In the invention, the inventors use spectrophotometry as a means of distinguishing between active polysulphide and inactive polysulphide.

The present invention is further based on the finding that there are previously unrecognized conditions that are necessary to ensure the highest level of **active** polysulphide and that these conditions can be different from the conditions that would give the highest **total** polysulphide concentration.

Dorris et al

The principal reference, Dorris et al, is concerned with oxidation of white liquor in the presence of lime mud. This oxidation is carried out employing oxygen, and as a consequence, sulphide in the liquor is oxidized. Some sulphide is oxidized to polysulphide, and some is oxidized to thiosulphate, as clearly explained by Dorris et al.

Reference has been particularly made to column 9, lines 24-25 which is part of Example 1. Column 9 of Dorris et al describes a series of tests carried out in Examples 2 to 6, to illustrate the effectiveness of varying different parameters, on the rate of sulphide oxidation and on the selectivity of lime mud under different operating conditions towards polysulphide generation. These Examples 2 to 6 particularly identify different polysulphide efficiencies. It is indicated that an efficiency of about 100% indicates that all sulphide was oxidized to polysulphide whereas an efficiency lower than 100% reveals oxidation to form both polysulphide and thiosulphate.

In the Office Action bridging pages 3 and 4, reliance is made on column 9, lines 24-25, which, it is indicated, teaches increasing the temperature of an oxidized white liquor from 90 to 100°C to complete the reaction and then storing. With respect, this is not what is described at column 9, lines 24-25. At column 9, lines 19-23, there is described the process of causticizing green liquor having an initial temperature of 90°C. This is **not** an oxidation process. It is a process for producing white liquor from green liquor. What is indicated at column 9, lines 24-25 is that at the end of the "causticizing", the white liquor temperature has increased from 90°C to 100°C as a result of the exothermic reaction of lime hydration. This white liquor is **not** oxidized white liquor. Column 9 indicates that a sample is removed for analysis, and this sample was the "zero time oxidation sample". In other words, this is a sample of the white liquor **before** the oxidation reaction commences. Thereafter, as described at column 9, lines 29 et seq., air or oxygen was introduced "to permit the oxidation reaction to proceed". It is indicated that the temperature during the oxidation ranged normally between about 100 to 104°C. These oxidations were carried out employing the different operating conditions of Examples 2 to 6, and it can be seen that the polysulphide efficiency was different in the different Examples based on the different operating parameters. Thus, in Example 2, the polysulphide efficiency was only 30%, the major product of oxidation being sodium thiosulfate rather than polysulphide.

Thus, with respect, the premise on which the objection based on Dorris et al is based is not correct.

In the first sentence at page 4 of the Office Action, it is indicated:

"It would have been obvious to the routineer that this further reaction would increase the concentration of the polysulfide."

First, the increase from 90 to 100°C in Dorris et al is not a further reaction. This increase in temperature is part of the causticizing reaction **prior to** the oxidation reaction.

The Examples demonstrate that the oxidation of the white liquor produced different amounts of polysulphide (i.e., different polysulphide efficiencies) depending on the operating parameters.

In fact, the Examples in the present application demonstrate that total polysulphide concentration decreases with time. Consequently, contrary to the assertion that it would be obvious to the routineer that a further reaction would

increase the concentration of the polysulphide, it is clear that increasing the temperature and then storing can, in fact, decrease the total polysulphide concentration as normally measured. By way of example, Table 4 at page 19 in the present specification shows that at 78°C the highest  $PS_{UV/VIS}/PS_{GR}$  ratio is obtained after 24 hours even though the  $PS_{GR}$  concentration (i.e., total polysulphide) in column 4 is decreasing and even the  $PS_{285}$  has decreased to some extent. Similar results can be seen in Table 8 at a temperature of 90°C.

Thus, in practice, the total polysulphide content decreases with time and temperature rather than increasing as suggested in the Office Action. On the other hand, with increase in time and temperature, the active polysulphide content of the total polysulphide increases.

Prior to the present invention, there was, of course, no recognition that polysulphide comprised two forms of polysulphide, one active and one inactive, in pulping, and clearly none of the cited references demonstrates this.

Furthermore, and contrary to the indication in the Office Action that increase in concentration of polysulphide is an obvious expectation of the routineer, with further reaction, the contrary is established in the art. Indeed, while it might normally be expected that, once the liquor is no longer within the reactor zone where the catalyst and oxygen needed for reaction are provided, no more polysulphide will be formed. Instead, as recognized in the literature and as shown in the Examples, the total polysulphide concentration decreases with time because of the **thermal** instability of the molecule.

The inventors found that some of the inactive polysulphide upon storing for appropriate times and at appropriate temperatures, as claimed in the application, is converted into active polysulphide and that this heat treatment overwhelms any decomposition of polysulphide that might otherwise be expected under the same conditions.

In accordance with the present invention, the application of heat treatment to an oxidized white liquor results in an improvement in the pulping yield of the polysulphide liquor as a result of increased concentration of active polysulphide within the total polysulphide content of the liquor.

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This is clearly not even hinted at by Dorris et al which neither recognizes the existence of the two forms of polysulphide nor that the content of the active polysulphide increases as a proportion of the total polysulphide under the heat treatment of the invention.

Secondary References

None of the secondary references in any way overcomes the basic failing of Dorris et al.

That the secondary references describe spectral analysis to measure sulphide concentrations in pulping liquids is immaterial. Neither Dorris et al nor the secondary references were aware of there being two forms of polysulphide with one being active and the other inactive or that the proportion of active polysulphide within the total polysulphide could be increased by the heat treatment of the invention.

In accordance with the invention, the concentration of active polysulphide at the expense of inactive polysulphide, within the total polysulphide, is increased. There is nothing in any of the references indicating this, and nothing that would teach, following the practices of the present invention, obtaining the indicated benefit of providing an oxidized white liquor exhibiting improved pulping yield characteristics.

In the light of the foregoing, reconsideration is requested.

Claims 15 to 18, which appear to have been overlooked, serve to further define the methods of the invention, and favourable consideration of these claims is requested.

The attached PAIR page with the file history of the application also shows in items 16 and 15 the second preliminary amendment of November 20, 2003 and, therefore, it is assumed that the amendment to the specification and drawings therein has been entered.

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The application is believed to be in condition for allowance, and early and favourable action would be appreciated.

Respectfully,

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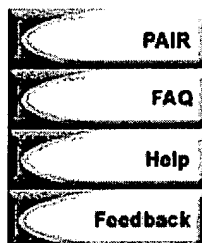
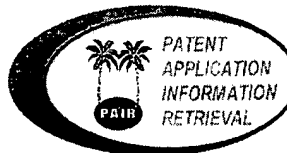




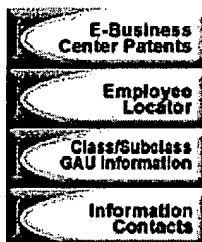
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Title Of Invention:	Kraft pulp yield by heat treatment of polysulphide liquors gen by oxidation		

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17	03-10-2004	Preliminary Amendment
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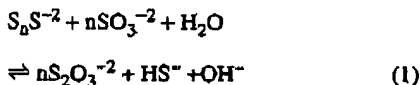
# Analysis of Oxidized White Liquors. Part I: Determination of Polysulphides by Gravimetry

G.M. DORRIS and V.C. ULOTH

*A gravimetric method for measuring polysulphide sulphur (PS) concentration in unoxidized and oxidized samples of white liquor is described. It is based on the precipitation of elemental sulphur when polysulphide solutions are acidified. The method was shown to be accurate enough for routine analyses. However, with certain types of liquors produced by oxidation with oxygen under pressure, the polysulphides concentrations were found to be affected by the degree of dilution during the acidification step.*

## INTRODUCTION

With the recent advent of polysulphide cooking in many kraft mills, there is a need to rapidly measure polysulphide concentrations in oxidized white liquor samples at a mill site. Many direct and indirect methods for polysulphide determination have been reviewed in the literature [1-2]. Indirect methods for kraft liquor analyses are based largely on the reaction of sulphite ions with polysulphide ions,  $S_nS^{2-}$ , according to:

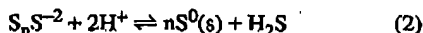


By measuring the thiosulphate concentration before and after the addition of sulphite to a liquor sample, the polysulphide concentration can be determined, since many potentiometric [3,4], iodometric [5], polarographic [6], and ion chromatographic [7] methods are available for thiosulphate determination in green or white liquors. Redox [8] and acidimetric [9,10] titration also

based on Reaction 1 can also be used to determine polysulphide concentrations. A potentiometric titration of sulphide ions with  $HgCl_2$  after reduction with sodium amalgam [1] and a thermometric [11] titration are also applicable for polysulphide determination. The procedures used in these methods are often elaborate and require equipment not always available at a mill site.

More direct measurements of polysulphide can be made by UV spectroscopy [12] and gas chromatography [13]. The spectrophotometric method is quite rapid but, at the large dilutions required for absorbance measurements, careful exclusion of air and control of the hydroxyl concentration and ionic strength are essential to obtain stable and reliable absorbance readings. Moreover, it has been reported that this method is not suitable for oxidized white liquor samples with a varying ratio of polysulphide sulphur to total sulphide sulphur [14].

The gas chromatographic (GC) method is claimed to be less sensitive to these techniques. It is based on the decomposition of polysulphide to elemental sulphur in a buffered aqueous solution (pH 5.5) according to the following reaction:



The precipitated elemental sulphur, which has a very low solubility in water, can be derivatized with triphenylphosphine and collected in a toluene extract. The product of the reaction, triphenylphosphine sulphide, is then determined by flame ionization GC on a packed column. The sample preparation technique is quite simple but the analysis time on a packed column is rather long. It is possible, however, to reduce the chromatographic analysis time from 20 to 2 min by the use of short capillary columns instead of packed columns [15]. The GC technique is

thus believed to be a convenient method for the concurrent analysis of large numbers of liquor samples and has, indeed, been used widely in this laboratory. The formation of sulphur is not new as early methods to measure polysulphides in sulphur chalk relied on the decomposition of polysulphide in slightly acidic media [16]. Recently, sulphur produced by acidification of polysulphide has been measured turbidimetrically by a flow injection technique [17].

Since a UV spectrophotometer or a gas chromatograph is not always available at the mill sites, we have used Reaction 2 as the basis for a gravimetric analysis of polysulphide sulphur in unoxidized and oxidized white liquors. The gravimetric method was tested with synthetic polysulphide liquors and with white liquor samples oxidized in the laboratory, by comparing its results with those obtained by gas chromatography and by the amalgam method described in the official TAPPI Test Method T 694 om-90. The advantages and limitations of gravimetry will be discussed in this paper.

## EXPERIMENTAL Preparation of Liquors

Synthetic polysulphide liquors were prepared by dissolution of elemental sulphur in two stock solutions under a nitrogen atmosphere. The first liquor (A) had a composition very similar to a mill white liquor. It was made by dissolving reagent grades NaOH (95 g),  $Na_2S \cdot 9H_2O$  (120 g) and  $Na_2CO_3$  (17 g) in deoxygenated distilled water to form a 1 L solution. One litre of a second liquor (B), used principally to prepare GC standards, was prepared by adding 150.0 g of  $Na_2S \cdot 9H_2O$  to deoxygenated distilled water. Synthetic polysulphide liquors of various concentrations were obtained by dissolution, with stirring, of ~0.2 to 4.0 g of elemental sulphur (99.999% pure

J<sub>P</sub>  
P<sub>S</sub>

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from Aldrich, weighed accurately) into 100 mL volumes of each of the two liquors held at 50°C in a nitrogen atmosphere. The resultant polysulphide liquors, with concentrations of polysulphide sulphur ranging between ~2.0 and 40 g/L, were then transferred to 50 mL serum bottles which were completely filled, capped with PTFE-lined septa and crimped aluminum seals [13].

Oxidized white liquors were prepared in a 1 L laboratory reactor, in a 1000 L pilot plant batch reactor and in a 150 m pipeline reactor. In the batch reactors, the oxidations were carried out at atmospheric pressure with air or oxygen, catalyzed by lime mud and/or MnO<sub>2</sub>. In the pipeline reactor, the operating pressure was as high as 1150 kPa at a maximum flow rate of 225 L/min. Details of the reactors and of the results of the trials will be presented elsewhere.

### Polysulphide Determination Gravimetry

A 10.0 mL volume of clear liquor was transferred by pipette into 100 mL of distilled water in a 250 mL beaker equipped with a magnetic stirrer. Although a 10 mL volume of liquor will normally yield sufficient precipitate to be accurately weighed, this volume may be increased to 25–50 mL for unoxidized mill liquors having a very low polysulphide concentration. With improperly clarified liquor, the contribution of finely dispersed calcium carbonate, or of co-precipitates containing multivalent metals, to the weight of precipitated sulphur may be significant. This source of error was found to be largely eliminated by the addition of a 10 mL of 0.05 M EDTA solution to the diluted liquor sample. The beaker was then placed in a fume hood and a combination glass pH electrode inserted in the beaker. Using a Pasteur pipette, the sample was rapidly acidified to a pH of 8 with HCl (3 mol/L) and constant agitation. The pH was then adjusted to 5.0–5.5 with HCl (1 mol/L). The solution then had a milky white appearance as a result of the finely divided elemental sulphur. A 4.7 cm diameter Millipore-type GS filter with a pore size of 0.22 µm, weighed on an analytical balance without drying, was fitted on a 4.7 cm Millipore filter holder to filter the fine precipitate. The filter assembly was mounted on a 250 mL filtering flask which contained a solution of NaOH (0.1 mol/L, 100 mL) to reduce H<sub>2</sub>S emission. The whole slurry was filtered under vacuum. Small aliquots of distilled water (a total of 50 mL) were used to transfer the precipitate quantitatively to the filter. After dewatering, the precipitate was washed with an additional 25 mL of distilled water and dewatered again under vacuum. At this stage, the wet precipitate should have a yellow colour. If it was grey, a 10 mL volume of 0.05 M EDTA followed by 10 mL distilled water was passed through the solid. Using a pair of tweezers, the membrane filter was transferred to a watch glass for drying. Because the drying conditions markedly affect the reproducibility of the results, it is preferable, when many samples are ana-

lyzed, to precipitate them consecutively and then dry all the samples simultaneously. Above 40°C, significant loss of sulphur on the filter was experienced. Best results were obtained by placing the samples in a vacuum desiccator for 2 h, although this method is not very practical. Drying at 80°C for exactly 20 min was found acceptable as, under these conditions, all the water is removed and sulphur loss by vaporization is very small.

During the filtration, washing and drying steps, the filter membrane lost between 0.4 and 0.6 mg. An average negative correction of 0.5 mg was therefore applied to the original weight of the filter. The concentration of polysulphide sulphur (PS) in g/L was then calculated from the difference between the dry weight of the membrane filter with the precipitated sulphur and the corrected weight of the filter, divided by the volume of liquor acidified.

The gravimetric method is rapid compared to most other methods as one person can easily analyze six samples in less than 90 min.

### Sodium Amalgam Method

This method (the official TAPPI Test Method T 694 om-90) is based upon the reduction of S<sub>8</sub>S<sup>2-</sup> to S<sup>2-</sup> by the sodium amalgam. As discussed by Easty and Johnson [18], the TAPPI procedure must be carefully followed to minimize the sources of error. Indeed, the results obtained by this method were found to depend greatly on the degree of dilution of the sample, its time of exposure to the amalgam, and the presence of air during the reduction. Precautions were taken to minimize the effect of these sources of error and only fresh amalgam samples were used for the reductions.

### Gas Chromatography

Sample preparation techniques and chromatographic conditions of the GC method have been described in detail by Borchardt and Easty [13]. To reduce the

analysis time, a short capillary column was substituted for the packed column suggested in the original method.

GC analysis was performed on a Hewlett-Packard 5880A equipped with a flame ionization detector and a 2 m × 0.25 mm DB-1 fused silica capillary column (J & W Scientific) [15]. The column oven temperature was 215°C and both the injector and detector ports were maintained at 260°C. Helium (high purity grade, further purified to remove traces of water and oxygen) was used as carrier gas at a linear column flow rate of ~25 cm/s. The solvent-flush technique was used to inject a 1 µL sample into the unpacked, deactivated split liner. The split ratio in the injector was kept at ~100:1. A typical chromatogram, shown in Fig. 1, indicates that the analysis time was ~1.5 min instead of the 20 min necessary in a packed column.

To produce good sized peaks with a 1 µL sample volume and a split ratio of 100:1, the sample preparation technique of Borchardt and Easty [13] was modified slightly. Volumes of 40 mL potassium acid phthalate buffer (pH 5.5) and 10 mL toluene containing the GC internal standard (i.e., tetracosane, 99%, from Aldrich, at a concentration of about 0.300 mg/mL) were placed in a 60 mL serum bottle. After purging with nitrogen, the bottle was capped with a PTFE-lined septum and crimped aluminum seal. One millilitre of triphenylphosphine (TPP, 99%, from Aldrich) at a concentration of 20 mg/mL was injected into a capped bottle, followed by an injection in the aqueous phase of 250 µL of liquor sample. Because the sample volume is ~5 times larger than in the original method, the buffer capacity was exceeded. Thus, an additional 1 mL of 1 mol/L HCl was also injected into the capped bottle to maintain the pH in the correct range. The bottle was then shaken for 10 min in a horizontal shaker and, after letting the two phases separate, 1 mL of the toluene phase was removed for GC analysis.

Because the response of the FID to triphenylphosphine sulphide (TPPS) and to

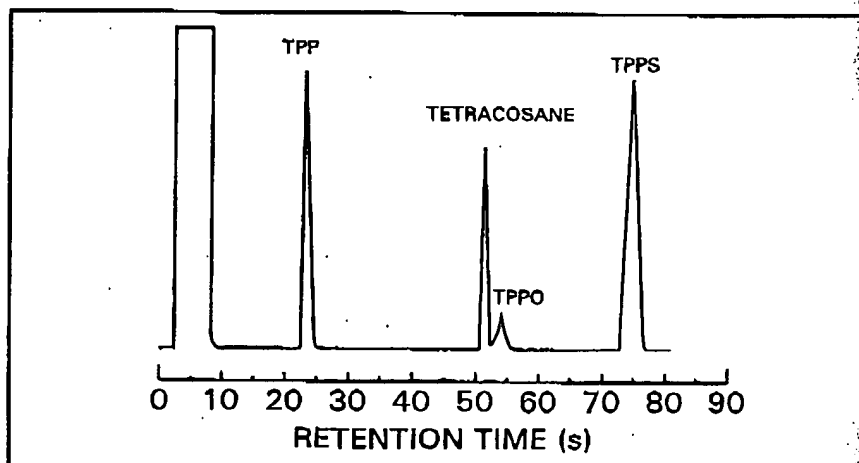


Fig. 1. Gas chromatogram of the toluene extract of an oxidized white liquor treated by the triphenylphosphine (TPP) method. (TPPO = triphenylphosphine oxide; TPPS = triphenylphosphine sulphide).

the internal standard, tetracosane, is different, a response factor (i.e., factor by which the area of the TPPS peak must be multiplied to give an equivalent weight of internal standard) was established by injecting mixtures with known compositions of TPPS (98% purity from Aldrich) and tetracosane. The polysulphide sulphur for each sample was determined from a minimum of two injections.

## RESULTS AND DISCUSSION

### Synthetic Liquors

Four polysulphide solutions, prepared by dissolution of elemental sulphur in two liquors (A and B), were analyzed by gravimetry, chromatography, and potentiometry with  $\text{HgCl}_2$  after reduction with a sodium amalgam. The results (Table I) indicate that sulphur recoveries by gravimetry range between 93 and 105%. Within the limits of precision of each method, there is a reasonably good agreement between the three methods. However, the sodium amalgam method is the least convenient for routine analysis because many precautions are required to maintain the integrity of the sample during analysis. Moreover, the manipulation and regeneration of fresh amalgam samples make this technique rather tedious. The poor reproducibility of the GC method was caused by variability in the relative peak areas of TPPS and the internal standard, induced by the split injection mode [19]. This source of imprecision can be reduced by the use of a packed column but the major gain in analysis time achievable with short capillary columns largely offsets the small loss of precision. Measurements of polysulphide sulphur by GC were therefore based on the mean of at least two injections. The results in Table I also suggest that, at least for these synthetic polysulphide solutions, gravimetry is a satisfactory method, with a maximum standard deviation of 0.2 g/L for concentrations ranging from 2 to 8 g/L.

### Oxidized White Liquors

Oxidized white liquor (OWL) samples were produced as described in the Experimental Section. Table II indicates that, with unoxidized liquors (A) and with liquors oxidized at atmospheric pressure in a batch reactor (OWL A, B and C), polysulphide sulphur concentrations measured by gravimetry and chromatography agree well. The results obtained with the sodium amalgam tend to be lower, possibly because contact of the dilute sample with air during the amalgam treatment and during titration was not totally prevented, thus causing sulphide losses which resulted in too low values of polysulphide sulphur in the determination. Easty and Johnson [18] have suggested the presence of inherent sources of errors in the sodium amalgam procedure. However, it is possible that gravimetry and chromatography, which are both based on the decomposition of polysulphide under acidic conditions, are also subject to error. A potential

source of error was indeed revealed when white liquors oxidized under pressure (OWL<sub>p</sub>, D, E and F) were analyzed both by gravimetry and by chromatography. As illustrated in Table II, gravimetry consistently yielded much higher values. Extraction with toluene of the material

precipitated during the gravimetric analysis indicated that the solid being weighed was only elemental sulphur with no impurities. As the major difference between the two techniques lay in the degree of dilution of the sample during acidification, the GC analyses on liquor samples D and E in Table II were repeated using the same dilution as that used in the gravimetric method. The values in parentheses in Table II indicate that the two methods then agreed. Thus, the degree of dilution of the polysulphide solutions appears to affect the amount of sulphur released during the acidification of white liquors oxidized under pressure.

This effect of dilution on the gravimetric results was studied further on three different samples. The first was a synthetic polysulphide liquor prepared by dissolution of 4 g of elemental sulphur in a 1 L volume of white liquor A. The other two were obtained from pilot plant runs during which mill white liquors were oxidized at atmospheric pressure in a batch reactor (OWL), and under pressure in a pipeline reactor (OWL<sub>p</sub>), respectively. Aliquots of 1, 5, 10 and 20 mL of each liquor were diluted in 100 mL of distilled water, acidified to pH 5, and

the released sulphur was measured by gravimetry. Table III shows that, at a sample volume equal to or larger than 5 mL, the polysulphide sulphur concentrations for the synthetic liquor and for the OWL sample are reasonably constant. In both cases, a 1 mL sample yields lower values because, with this small (4 mg of sulphur) sample, small losses occurring during filtration have a significant effect on the weight of sulphur determined. The effect of dilution on the determination by gravimetry appears to be small for these two types of polysulphide liquors. In contrast, the amount of elemental sulphur released by the acidification of a 1 mL sample of white liquor oxidized under pressure (OWL<sub>p</sub>) is far too low, compared to the larger size samples, to be accounted for by material losses during sample filtration.

Because a shift in the complex equilibria between various sulphur anions is more likely to occur when the sample is more dilute, determination of polysulphide sulphur by gravimetry should be more reliable when larger sample sizes are used in the acidification step. However, colour changes occurring during acidification indicated that this argument might not be correct for liquor

TABLE I  
COMPARISON OF DIFFERENT METHODS FOR THE DETERMINATION OF POLYSULPHIDE SULPHUR IN SYNTHETIC LIQUORS

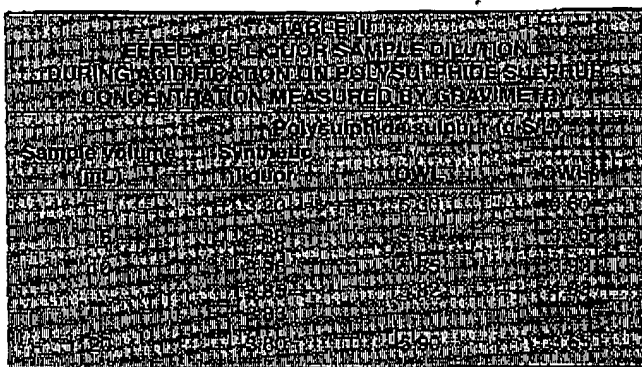
Samples	Gravimetry	Chromatography	Sodium Amalgam
Synthetic liquor A	7.8 (0.2)	7.6 (0.2)	7.5 (0.2)
Synthetic liquor B	2.5 (0.1)	2.4 (0.1)	2.3 (0.1)
Synthetic liquor C	5.1 (0.1)	5.0 (0.1)	4.9 (0.1)
Synthetic liquor D	1.2 (0.05)	1.1 (0.05)	1.0 (0.05)
Synthetic liquor E	3.5 (0.1)	3.4 (0.1)	3.3 (0.1)
Synthetic liquor F	6.2 (0.2)	6.1 (0.2)	6.0 (0.2)

Values in parentheses are standard deviations. Values were obtained from two injections.

TABLE II  
COMPARISON OF DIFFERENT METHODS FOR THE DETERMINATION OF POLYSULPHIDE SULPHUR IN OXIDIZED LIQUORS AND IN LIQUORS OXIDIZED UNDER PRESSURE (OWL<sub>p</sub>) AND UNDER PRESSURE (OWL<sub>p</sub>)

Samples	Gravimetry	Chromatography	Sodium Amalgam
OWL A	7.8 (0.2)	7.6 (0.2)	7.5 (0.2)
OWL B	2.5 (0.1)	2.4 (0.1)	2.3 (0.1)
OWL C	5.1 (0.1)	5.0 (0.1)	4.9 (0.1)
OWL <sub>p</sub> D	1.2 (0.05)	1.1 (0.05)	1.0 (0.05)
OWL <sub>p</sub> E	3.5 (0.1)	3.4 (0.1)	3.3 (0.1)
OWL <sub>p</sub> F	6.2 (0.2)	6.1 (0.2)	6.0 (0.2)

Values in parentheses are standard deviations. Values were obtained from two injections.



samples oxidized under pressure. Synthetic polysulphide solutions or white liquors oxidized at atmospheric pressure had a yellow to orange colour, characteristic of polysulphide ions. Upon acid addition, the colour disappeared only when the precipitation of elemental sulphur was complete at a pH of around 6. In contrast, almost all liquors partially oxidized in the pressurized pipeline reactor had a pale green colour. After dilution and acidification to pHs between 10 and 12, the solutions turned yellow. UV spectra on liquor samples taken during acidification indicated the presence of the characteristic polysulphide bands. The band vanished rapidly unless the pH of the solution was brought down to ~8. Thus, the appearance of the yellow colour upon acidification appears to be due to the formation of polysulphide as the alkalinity dropped. These observations suggest that polysulphides in liquors oxidized under pressure were not present in significant quantities in the undiluted liquors but rather were formed during the acidification because of a shift in one of the many equilibrium reactions involving the various sulphur species in solution. One possible cause for the observed phenomenon will be discussed in a future paper.

The results of a gravimetric analysis for polysulphide should thus be interpreted with caution as this method appears to yield erroneous results for certain liquors, such as white liquor oxidized with oxygen under pressure at elevated temperatures. To ensure reliable results, gravimetric analyses should be carried out with different sample sizes. In case of discrepancy, the test should be repeated at progressively higher dilutions (up to water/sample > 100) but with larger sample sizes to produce enough sulphur to be weighable.

## CONCLUSIONS

A gravimetric method based on acidification to produce elemental sulphur is effective for routine analyses of polysulphide sulphur (PS) in oxidized white liquor. However, in liquors oxidized with oxygen under pressure the concentrations of PS were affected by the degree of dilution of the samples before they were acidified. This problem can be avoided by carrying out the gravimetric test on samples diluted to different degrees.

## ACKNOWLEDGEMENTS

The authors wish to thank Natalie Pagé, Sylvain Martineau and Michelle Ricard for their careful technical assistance and T. Galvin for the production of pilot plant samples. J. Sullivan is thanked for establishing conditions for the gas chromatographic technique.

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**REFERENCE TO OTHER WORK:** A method for the determination of polysulfide sulfur in white liquor by gravimetry is described. The method involves the acidification of the sample to produce elemental sulfur, which is then weighed. The results are compared to those obtained by a standard method. The method is shown to be effective for routine analyses of polysulfide sulfur in white liquor. However, in liquors oxidized with oxygen under pressure the concentrations of PS were affected by the degree of dilution of the samples before they were acidified. This problem can be avoided by carrying out the gravimetric test on samples diluted to different degrees.

**ABSTRACT:** A gravimetric method for the determination of polysulfide sulfur in white liquor is described. The method involves the acidification of the sample to produce elemental sulfur, which is then weighed. The results are compared to those obtained by a standard method. The method is shown to be effective for routine analyses of polysulfide sulfur in white liquor. However, in liquors oxidized with oxygen under pressure the concentrations of PS were affected by the degree of dilution of the samples before they were acidified. This problem can be avoided by carrying out the gravimetric test on samples diluted to different degrees.

**RESUME:** Une méthode gravimétrique pour la détermination du soufre polysulfidés dans le blanc de soufre est décrite. La méthode implique l'acidification de l'échantillon pour produire du soufre élémentaire, qui est ensuite pesé. Les résultats sont comparés à ceux obtenus par une méthode standard. La méthode est montrée être efficace pour les analyses de routine du soufre polysulfidés dans le blanc de soufre. Cependant, dans les liquors oxydés avec l'oxygène sous pression, les concentrations de PS étaient affectées par le degré de dilution des échantillons avant qu'ils ne soient acidifiés. Ce problème peut être évité en effectuant le test gravimétrique sur des échantillons dilués à différents degrés.

**KEYWORDS:** WHITE LIQUOR; POLYSULFIDES; GRAVIMETRIC ANALYSIS; ACIDIFICATION; ELEMENTAL SULFUR; Sulfur; Polysulfide; White liquor; Polysulfide; Gravimetric analysis; Acidification; Elemental sulfur.



# Analysis of Oxidized White Liquors. Part II: Potentiometric Titrations for the Determination of Polysulphides and Sulphoxy Anions

G.M. DORRIS and V.C. ULOTH

*When acidimetric titrations ("ABC" method) were carried out on liquors with concentrations of polysulphide sulphur (PS) greater than ~2g S/L, a new endpoint around a pH of 8 was shown to appear. This endpoint, which occurs because of incomplete reaction between polysulphide and formaldehyde, was used to get a measure of PS concentration. Alkali changes during oxidation of sulphide ions were shown to be caused by concurrent formation of polysulphide, thiosulphate, and sulphate ions.*

## INTRODUCTION

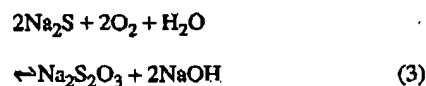
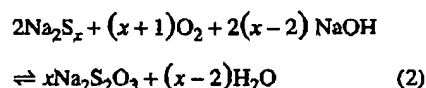
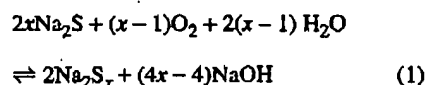
It was shown previously [1] that a simple gravimetric method may be used to determine routinely polysulphide concentrations in oxidized white liquors. Since most mills already analyze their white liquors by the so-called standard ABC titration, some problems associated with the use of this titration on polysulphide liquors have been identified and will be discussed in this second paper of a two-part series.

Because partial oxidation of white liquor samples for polysulphide generation is claimed to result in an increase in effective alkali concentration [2,3] and because the alkalinity of green and white liquors is routinely measured at mills by the standard ABC titration, an attempt was made to relate changes in the alkali concentrations, as white liquor oxidation proceeds, to polysulphide production. It will be shown that these changes during oxidation produce useful information not only on polysulphide forma-

tion but also on the concurrent thiosulphate and sulphate generation.

## CHEMICAL EQUILIBRIA OF OXIDATION SPECIES

The conventional way of expressing the various oxidation reactions involving sodium sulphide in white liquor is given in the following reactions [2,4,5]:

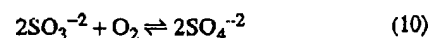
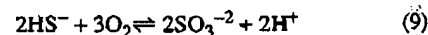
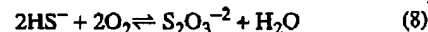
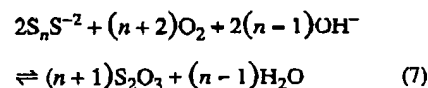
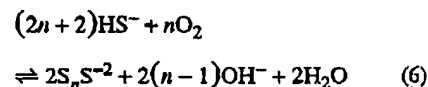


where  $5 \geq x \geq 2$  in Reactions 1 and 2.

These equations suggest that caustic soda is always produced during the formation of thiosulphate or polysulphide by direct oxidation of sodium sulphide (Reactions 1 and 3). This is misleading because the ion,  $\text{S}^{2-}$ , does not participate in the oxidation reaction. Indeed, it is now well established that the sulphide ions in green, white or black liquor are completely hydrolyzed to sodium hydrosulphide by the reaction [6,7]:



Thus the NaOH apparently produced by the oxidation Reactions 1 and 3 comes largely or solely from the hydrolysis reaction and is produced independent of any oxidation reaction. When the oxidation reactions are expressed in terms of hydrosulphide rather than sulphide ion [8], and when the polysulphide ions are expressed as  $\text{S}_n\text{S}^{2-}$  instead of  $\text{S}_x^{2-}$ , the most important oxidation reactions involved are:



where  $4 \geq n \geq 1$  in Reactions 6 and 7.

The stoichiometry of these reactions indicates that formation of thiosulphate does not produce or consume caustic. Further oxidation of hydrosulphide ions to sulphite and finally to sulphate ions consumes 1 mol of  $\text{OH}^-$  per mole of  $\text{SO}_4^{2-}$  formed. The caustic balance accompanying polysulphide formation is more complex because it depends on the chain length,  $n$ , of the polysulphide sulphur,  $\text{S}_n$ , of zero oxidation state being formed during the oxidation. The equilibria of polysulphide solutions have been thor-

J<sub>PPS</sub>

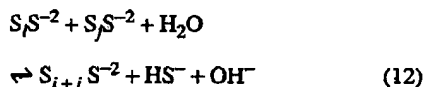
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oughly studied by Teder [9,10] and Giggenbach [11,12]. Although their studies were not made on oxidized liquors but on polysulphide solutions produced by dissolution of sodium tetrasulphide or of sulphur in aqueous hydroxide and sulphide solutions, their observations also apply to oxidized white liquors.

When sulphur is added to an alkaline sulphide solution, the equilibrium between elemental sulphur and polysulphide ions of average chain length,  $\bar{n}$ , can be written as:



Thus, hydroxyl ions are consumed in the formation of polysulphide by sulphur dissolution. The average size,  $\bar{n}$ , indicates that many polysulphide ions of various sizes can be simultaneously present in solution. The equilibria between polysulphide ions of different sulphur chain lengths in aqueous solutions can generally be described by the equation [13]:



The proportion of the various polysulphide ions in equilibrium is controlled by the variable B [10]:

$$B = \frac{[HS^-][OH^-]}{[S(0)]} \quad (13)$$

Spectroscopic observations indicate that the average  $\bar{n}$  value of a mixture of polysulphide ions ( $S_2S^{2-}$ ,  $S_3S^{2-}$ ...) tends to decrease with increasing B value [10] and temperature [12]. The equilibrium distribution of polysulphide ions as a function of B values, presented by Giggenbach [11,12], suggests that, with the high degree of alkalinity present in oxidized white liquors, the following polysulphide ions are present:  $SS^{2-}$ ,  $S_2S^{2-}$ ,  $S_3S^{2-}$  and  $S_4S^{2-}$ . According to the stoichiometry of Reaction 6, when  $n$  equals 1, 2, 3, or 4 the amount of caustic produced by the oxidation of hydrosulphide to polysulphide ions would be 0, 0.33, 0.5 or 0.6 mol, respectively, per mole of  $HS^-$  oxidized. Thus, provided that the average  $\bar{n}$  value of the polysulphide ions is larger than 1, hydroxyl ions will indeed be produced when polysulphide ions are formed.

Because of the rearrangement between polysulphide ions of various sizes (Reaction 12), analysis of polysulphide ions, once they are diluted and/or titrated with acid, is not straightforward. During acidification the polysulphide ions rearrange to form fewer but larger polysulphide ions [13,14]. Although this rearrangement reaction is of technical importance, the equilibrium described by Reaction 11 is of more significance to the analysis of polysulphide sulphur by gravimetry, chromatography or acidimetry. Upon acidification, the hydrolysis of polysulphides ions will be forced (i.e., reaction goes to the left), causing the release

of 1 mol of  $OH^-$  and 1 mol of  $HS^-$  per mole of elemental sulphur precipitated. The basis of both the gravimetric and chromatographic methods, described previously [1] is thus the forced hydrolysis of polysulphide ions.

## EXPERIMENTAL

### Preparation of Liquors

Preparation of synthetic polysulphide liquors by dissolution of elemental sulphur in two stock solutions under a nitrogen atmosphere has already been described [1].

Oxidized white liquors were prepared in a laboratory reactor, in a 1000 L pilot plant batch reactor and in a pilot plant pipeline reactor. In the batch reactors, the oxidations were carried out at atmospheric pressure with air or oxygen, with various types of oxidation catalysts whereas, in the 150 m serpentine reactor, the operating pressure was as high as 1150 kPa for a maximum flow rate of 225 L/min.

### Liquor Analyses

#### Determination of sulphide, thiosulphate, sulphite and sulphate ions

Total sulphide (i.e., free sulphide plus sulphide bound in polysulphide) was determined, on 1 to 5 mL samples to which an excess of sodium sulphite was added, by a potentiometric titration with  $HgCl_2$  using a sulphide ion-selective electrode [15]. Thiosulphate was also determined from a potentiometric titration with  $HgCl_2$  but no sulphite was added prior to the titration; sulphide and polysulphide ions were first removed by titration with  $HgCl_2$  to an equivalence point located at ~500 to ~400 mV. The pH of the medium was then adjusted to 7.0–7.5 and formaldehyde added; the solution was then titrated to a second equivalence point (~-50 to -10 mV). The thiosulphate concentration was calculated from the volume of  $HgCl_2$  consumed between the two equivalence points.

These titrations, as well as acidimetric titrations to be described later, were all carried out at room temperature under a nitrogen atmosphere with a Metrohm 636 Titroprocessor using the dynamic mode of volume addition. The endpoints were identified by the automatic titrator.

It has been reported by Bilberg [16] and Papp [15] that, during the titration of thiosulphate with  $HgCl_2$ , sulphite ions were also titrated. To eliminate this interference, it was recommended to add formaldehyde in order to convert sulphite into an inert bisulphite compound. However, examination of the potentiometric titration curves for many mill liquor samples, spiked with sodium sulphite and/or sodium thiosulphate, indicated that the thiosulphate endpoint identified by the titroprocessor was not affected by the presence of sulphite ions. In a mixture of both ions, there are generally two endpoints on the potentiometric curve. The first one, which is relatively sharp and easily identifiable, at a potential of -50 to -10 mV, corresponds to thiosulphate titration; the second one, at a slightly positive electrode potential

(i.e. 70 to 130 mV), is ill-defined and corresponds to sulphite titration. Although formaldehyde addition improves the definition of the thiosulphate endpoint, it does not significantly change the value of the first endpoint volume identified by the titroprocessor. Thus, when an automatic titrator is used for the potentiometric determination of sulphur species in a liquor containing both thiosulphate and sulphite ions, the first endpoint corresponds to thiosulphate and not to thiosulphate plus sulphite. Because the second endpoint, corresponding to sulphite titration, is not well defined, the procedure of Bilberg [16], adapted by Papp [15] for a sulphide ion-selective electrode, is believed to be inaccurate for the determination of sulphite or even the sum of sulphite and thiosulphate.

Sulphite and sulphate ion analyses were performed on a Dionex Model 4000 ion chromatograph equipped with conductivity and UV detectors. The conditions used, as well as the problems associated with the analyses of sulphite ions, have been described in detail by Douek et al. [17].

### Polysulphide Determination by Gravimetry

A gravimetric method for measuring polysulphide sulphur concentration (PS) in unoxidized and oxidized liquor has been described in detail previously [1].

### Acidimetric Titrations

In most cases, 5 mL liquor samples diluted to 100 mL with distilled water were titrated potentiometrically with HCl (1 mol/L) using Technical Section, CPPA Standard J.5 (Standard ABC method). Some samples were also titrated using modified ABC procedures: without  $BaCl_2$  addition before the titration, and without formaldehyde after the first endpoint; with formaldehyde and  $BaCl_2$  added prior to the titration; without  $BaCl_2$  but with formaldehyde added after the first endpoint.

## RESULTS AND DISCUSSION

### Potentiometric Titrations

#### Acidimetric Titrations With and Without Formaldehyde Added

In a mill, the concentrations of hydroxyl, sulphide and carbonate ions in unoxidized green or white liquor are generally determined by a titration with acid according to procedures described in Technical Section, CPPA Standard J.12 or in SCAN 2:63. The three endpoints of the so-called ABC titration can be identified by using chemical indicators (SCAN) or inflection points on the potentiometric titration curve (CPPA). A typical potentiometric curve for an unoxidized mill white liquor is shown in Fig. 1. (Note that this liquor had a high thiosulphate concentration of 6 g/L, as  $Na_2O$ .) In this ABC titration procedure, an excess of barium chloride is added to the diluted liquor sample to precipitate the carbonate ions as insoluble barium carbonate which is neutral toward phenolphthalein. When the titration is carried out to the first equivalence point,



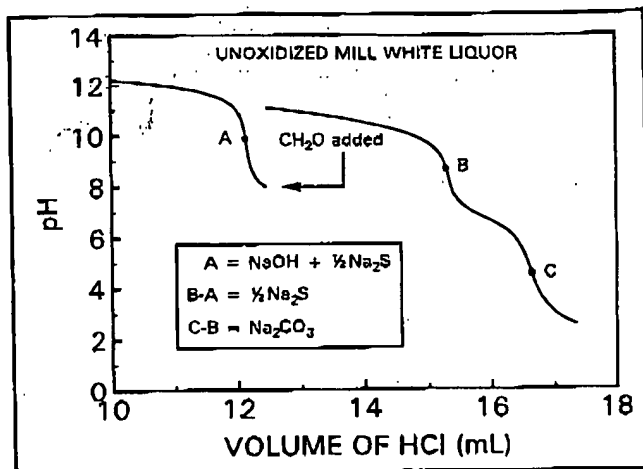


Fig. 1. ABC titration curve of a mill white liquor.

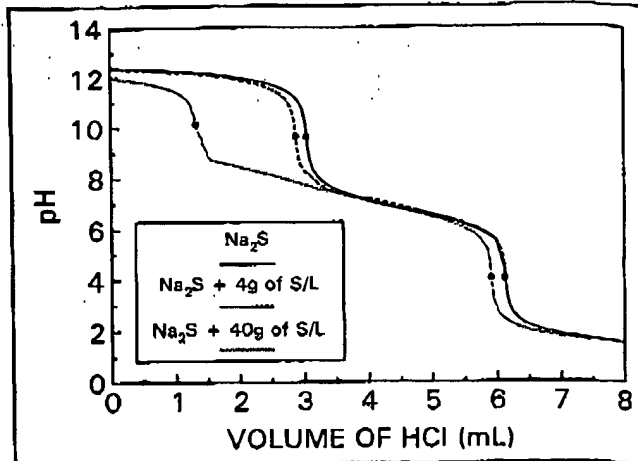


Fig. 2. Potentiometric titration curves of a pure sodium sulphide solution, before and after sulphur dissolution.

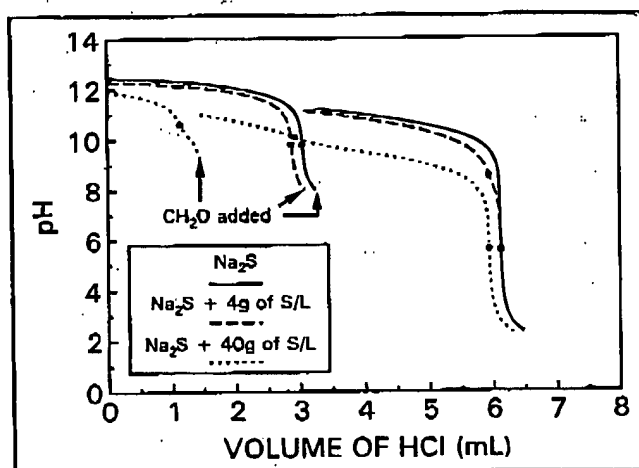
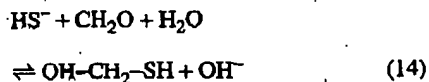


Fig. 3. Potentiometric titration curves of the same solutions in Fig. 2 with formaldehyde added after the first endpoint.

A, the hydroxyl ions produced by the causticizing reaction and by the hydrolysis of sodium sulphide (Reaction 5) are neutralized ( $A = \text{NaOH} + 0.5 \text{Na}_2\text{S}$  on a  $\text{Na}_2\text{O}$  basis). After this first endpoint, an excess of neutralized formaldehyde is added to convert  $\text{HS}^-$  into  $\text{OH}^-$  according to:



The released  $\text{OH}^-$  ions, which on a molar basis equal the  $\text{HS}^-$  concentration, are then titrated in going to the second endpoint, B ( $B - A = 0.5 \text{Na}_2\text{S}$  as  $\text{Na}_2\text{O}$ ). The titration is continued to a third endpoint, C, which represents the neutralization of the hydroxyl ions formed by hydrolysis of barium carbonate ( $C - B = \text{Na}_2\text{CO}_3$  as  $\text{Na}_2\text{O}$ ). From the amount of acid consumed at the three endpoints, the effective alkali ( $\text{EA} = \text{NaOH} + 0.5 \text{Na}_2\text{S}$ ), the active alkali ( $\text{AA} = \text{NaOH} + \text{Na}_2\text{S}$ ) and the total titratable alkali ( $\text{TIA} = \text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$ ) can all be determined.

This standard procedure has been modified by Ahlgren [19] to measure polysulphide sulphur in white liquors containing significant amounts of polysulphide. To estimate the polysulphide sulphur concentration, two separate titrations are required.

When Ahlgren's first acidimetric titration (i.e., addition of  $\text{BaCl}_2$  and formaldehyde before titration) was tried on oxidized white liquor samples, it was observed that, whenever these liquors had polysulphide sulphur concentrations in excess of  $\sim 2 \text{ g/L}$ , three endpoints, instead of the two predicted by Ahlgren, were consistently detected by the titroprocessor. By running titrations on the same sample with and without adding  $\text{BaCl}_2$  or formaldehyde, it was observed that this additional endpoint was detectable only when an excess of formaldehyde was added either before the titration or after the first endpoint. Thus, the reaction between polysulphide ions and for-

maldehyde appeared to be responsible for this new endpoint. To establish the origin of this new endpoint, a sodium sulphide solution was analyzed acidimetrically before and after dissolution of 4 and 40 g of elemental sulphur, respectively, in a 1 L volume of the stock sulphide liquor. The resulting solutions were obviously simpler to analyze than white liquors because there were no hydroxyl or carbonate ions from the causticizing reaction and virtually no sulphonyl anions.

From a potentiometric titration with  $\text{HgCl}_2$ , the sulphide concentration of the stock solution was found to be 39.0 g/L, as  $\text{Na}_2\text{O}$ . The polysulphide sulphur concentrations of the solution after addition of 4 and 40 g of sulphur were found gravimetrically to be 4.01 and 39.1 g of S/L. Figures 2 and 3 present pH titration curves of the sodium sulphide solution, before and after sulphur dissolution, without (Fig. 2) and with formaldehyde added after the first endpoint (Fig. 3). In Table I, the titrant volumes at the endpoints, indicated by filled circles in the two figures, are presented. With no formaldehyde added, only two endpoints were detected in the three solutions. The first inflection point on the  $\text{Na}_2\text{S}$  curve corresponds again to the neutralization of hydroxide ions produced by the hydrolysis of sulphide ions (Reaction 5) whereas the second one represents the neutralization of the hydroxyl ions produced by the hydrolysis of  $\text{HS}^-$  ions according to:

TABLE I ENDPOINT VOLUMES FOR 5 mL SAMPLES OF STOCK Na <sub>2</sub> S SOLUTIONS WITH AND WITHOUT SULPHUR ADDED, TITRATED WITH 0.2 N HCL (WITH AND WITHOUT FORMALDEHYDE ADDED AFTER THE FIRST ENDPOINT (A SEE FIGS. 2 AND 3 FOR pH CURVES))			
	Na <sub>2</sub> S	Na <sub>2</sub> S + 4g S/L	Na <sub>2</sub> S + 40g S/L
1st endpoint (mL)	2.5	2.5	2.5
2nd endpoint (mL)	5.5	5.5	5.5
3rd endpoint (mL)	-	6.5	6.5

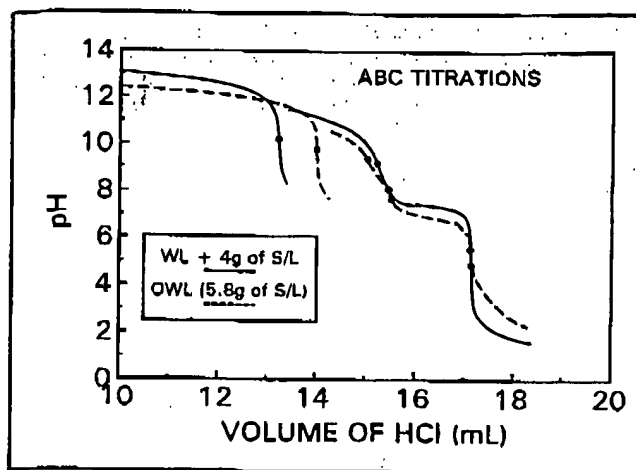
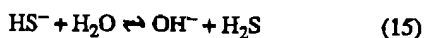


Fig. 4. Titration curves obtained by the standard ABC procedure on two white liquor samples.

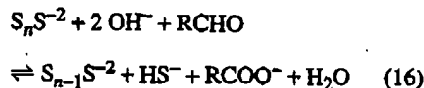


The use of the first and second endpoint volumes in Table I to calculate sulphide concentration in the stock liquor yields values of 39.0 and 39.1 g/L ( $\text{Na}_2\text{O}$ ), respectively, in excellent agreement with that measured by titration with  $\text{HgCl}_2$ . After sulphur addition, the volume at the first endpoint is reduced because polysulphide formation by sulphur dissolution consumes both  $\text{OH}^-$  and  $\text{HS}^-$  ions (Reaction 11). From the drop in  $\text{OH}^-$  concentration after sulphur addition and from the polysulphide sulphur concentrations, ( $\bar{n} = \Delta[\text{OH}^-]/[\text{S}(0)]$ ), it can be estimated that the mean size of polysulphide ions,  $\bar{n}$ , is  $\sim 3.3$  for both polysulphide solutions, in agreement with reported  $\bar{n}$  values at  $25^\circ\text{C}$  (i.e., 2.9 to 3.8 [11,20]). The pH curves of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S} + 4 \text{ g S/L}$  in Fig. 2 also show that, at the second inflection point, the titrant volume is the same for both solutions. Thus, although  $\text{OH}^-$  and  $\text{HS}^-$  are consumed during polysulphide formation, the same two ions eventually get liberated at a lower pH when polysulphide ions hydrolyze (i.e., Reaction 11 goes to the left). With a very high concentration of polysulphide, the titrant volume at the second endpoint is slightly lower than in the other two solutions. It is suspected that small amounts of thiosulphate ions, which are non-titratable by acid at high pHs, were formed during sample preparation.

As depicted in Fig. 3, formaldehyde addition after the first inflection point led to the appearance of a weak inflection point on the pH curves of polysulphide solutions. However, as shown in Table I, the third endpoint volume on the pH curves of polysulphides solutions treated with formaldehyde corresponds to the second endpoint on the pH curves without formaldehyde addition. Thus, the final endpoint on the pH curves obtained with or without formaldehyde addition can be used to estimate the total sulphide concentration (i.e., free + bound to polysulphide sulphur) in polysul-

phide liquors produced by dissolution of elemental sulphur in sodium sulphide solutions. The origin of the second endpoint after formaldehyde addition still remained unclear. According to Ahlgren [19], when an excess of formaldehyde is present, the sulphide ion,  $\text{S}^{2-}$ , in  $\text{S}_n\text{S}^{2-}$  consumes two hydrogen ions, as does the free sulphide. However, the curves shown in Fig. 2 and the data in Table I indicate that, without formaldehyde, the bound sulphide also consumes

two hydrogen ions during polysulphide hydrolysis. Because formaldehyde addition decolorized polysulphide solutions only partly, it was suspected that the reaction between  $\text{CH}_2\text{O}$  and  $\text{S}_n\text{S}^{2-}$  did not go to completion at room temperature. It has been reported [20] that, during a polysulphide cook, polysulphide ions are consumed by reaction with aldehyde groups in wood components before maximum pulping temperature is reached:



To check the extent of the reaction between polysulphides ions and formaldehyde, a 5 mL volume of the polysulphide solutions with 4.0 and 39.1 g/L of polysulphide sulphur, respectively, was treated with a 5 mL volume of formaldehyde. The two treated liquors were then acidified to pH 5.5 and the sulphur which precipitated below a pH of 8.5 was measured by gravimetry. Under the action of formaldehyde, the polysulphide sulphur concentrations in the two solutions dropped from 39.1 to  $\sim 30$  and from 4.0 to  $\sim 1.5$ , respectively. The gravimetric results confirm qualitatively at least that polysulphides are only partially attacked by formaldehyde at room temperature. This partial conversion is indeed responsible for the appearance of this second endpoint after the addition of formaldehyde. They also suggest that the species being titrated between the second and third endpoint in Fig. 3 are the hydrolysis products of polysulphides ions not decomposed by the action of formaldehyde to produce elemental sulphur and hydroxyl ions (Reaction 11). It remains unclear, however, why the difference in titrant volumes between the second and first endpoints is larger than the first endpoint volume in liquor containing polysulphide ions. The stoichiometry of Reaction 16 indicates that there should be a net loss of titratable species in the alkaline pH

range upon formaldehyde addition because 2 mol of  $\text{OH}^-$  are consumed per mole of  $\text{HS}^-$  produced by the abstraction of one polysulphide sulphur atom. The difference in precipitated sulphur on acidified liquor samples, before and after formaldehyde addition, would indeed suggest a loss of  $\sim 0.5$  mol  $\text{OH}^-$  per mole of  $\text{HS}^-$  formed.

However, if the mean  $\bar{n}$  of polysulphide ions after formaldehyde addition was constant, then the difference in titrant volume between the second and third endpoints could be used to estimate polysulphide sulphur concentration in oxidized liquors. This hypothesis was tested further by using analyses made on two other liquor samples, which contained carbonate and hydroxide ions as well as varying concentrations of oxidized sulphur anions (i.e.  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ). The first sample (WL + 4 g of S/L) was a laboratory white liquor to which elemental sulphur was added to produce a polysulphide sulphur concentration of 4.0 g/L. The second sample (OWL) was a mill white liquor oxidized with air at atmospheric pressure in a large stirred reactor, in the presence of lime mud particles; the polysulphide sulphur concentration determined by gravimetry was 5.8 g of S/L. These two liquors were then titrated with HCl using the standard ABC procedure. The potentiometric curves, shown in Fig. 4, indicate that the WL and OWL samples both exhibited four endpoints. As in the  $\text{Na}_2\text{S}$  solutions with sulphur added (Fig. 3), the titroprocessor identified at a pH of around 7.8–8.5 a weak inflection point on the OWL and WL + 4 g of S/L curves as a result of the reaction between polysulphides and formaldehyde (Reaction 16).

The effect of formaldehyde on the hydrolysis of polysulphide ions was studied further by measuring the amount of precipitated sulphur as the pH of the OWL sample was progressively reduced by acid additions, with and without formaldehyde added before the acidification. As shown in Fig. 5, the OWL sample without the addition of formaldehyde released elemental sulphur by hydrolysis of polysulphide ions between pHs 8 and 7. With formaldehyde addition, the total amount of polysulphide sulphur decreased from 5.8 to 3.6 g of S/L and the pH range of polysulphide hydrolysis increased. Indeed, the pH range where sulphur precipitated corresponds well to that between the second and third endpoints in the acidimetric titration curve of the OWL sample in Fig. 4. From the titrant volume between these two endpoints and from the amount of precipitated sulphur after formaldehyde addition (i.e., 3.6 g of S/L), the  $\bar{n}$  value of hydrolyzed polysulphide ions can be estimated to be about 2.5. It is important to note that this mean  $\bar{n}$  value does not necessarily represent the size of the polysulphide ions in the original solution, but rather that of the ions when they hydrolyze in the presence of formaldehyde upon neutralization.

Since the difference in titrant volume between the second and third endpoints on pH curves with formaldehyde added appears

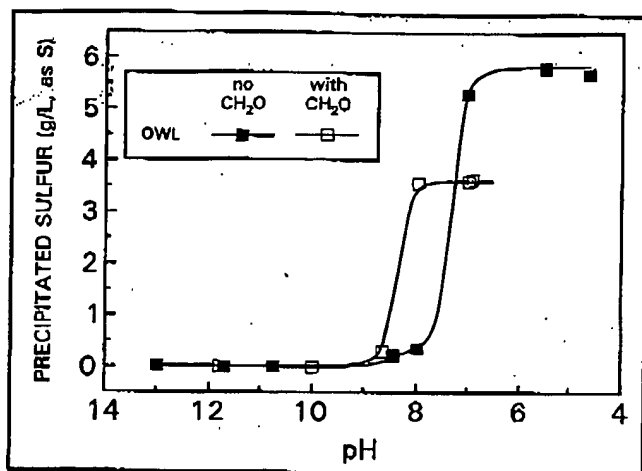


Fig. 5. Effect of pH on the amount of precipitated sulphur in a white liquor sample with and without formaldehyde addition before acidification.

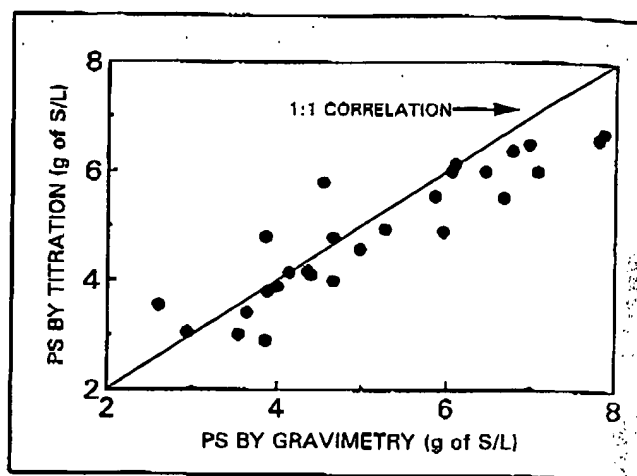


Fig. 6. Comparison between gravimetry and acid titration method (ABC procedure) for polysulphide sulphur determination in oxidized white liquor samples.

to truly represent the neutralization of bound sulphide ( $S^{2-}$  in  $S_nS^{2-}$ ) in OWL samples, it may indeed be possible to estimate polysulphide sulphur concentration from a single titration instead of the two titrations proposed by Ahlgren [19]. To do so, however, a mean  $\bar{n}$  value for all oxidized white liquors must be assumed. It was demonstrated that, after formaldehyde addition, the  $\bar{n}$  value of the OWL sample was around 2.5. If, as a first approximation, we assume from Reaction 16 that this  $\bar{n}$  represents  $(\bar{n} - 1)$  in the equation, then  $\bar{n}$  before the reaction of formaldehyde should be 3.5, when the hydrolysis reaction takes place. Figure 6 shows the polysulphide sulphur (PS) concentration in a number of oxidized white liquors measured by gravimetry and by acidimetry, with the assumption of a constant  $\bar{n}$  value of 3.5 for all samples. The agreement between the two methods is only fair, with the titrimetric method yielding in general lower results than gravimetry. If we consider that the titrant volumes used to estimate the bound sulphide range from 0.1 to 0.6 mL only, and that the assumption of a constant  $\bar{n}$  value of 3.5 may not be generally valid, the agreement is quite satisfactory. Thus, a rough estimate of PS concentration may be obtained from a single acidimetric titration using the ABC procedure provided that this concentration exceeds ~2 g of S/L and that the pH curves are generated by an automatic titrator. Nevertheless, gravimetry remains a much more accurate analytical method for polysulphide determination than an acidimetric titration.

From results presented so far, it can also be concluded that, if a mill carries out the routine ABC titration on oxidized liquors, the analysis of the curves will not be straightforward. When polysulphide ions are present, four and sometimes five endpoints, instead of the three in unoxidized liquors, can usually be identified. The first endpoint, A, is sharp and easily definable; it represents the hydroxyl ions from the causticizing reaction plus those from the hydrolysis of sulphide ions not bound to

polysulphide sulphur atoms ( $A = EA$ , the effective alkali). From the difference in titrant volumes between the first (A) and second (B) endpoints ( $B-A$ ), a rough estimate of free hydrosulphide ions,  $HS^-$  (or 0.5  $Na_2S$ ) can be made. The free sulphide ions can thus be obtained by multiplying ( $B-A$ ) by two. The bound sulphide concentration,  $S^{2-}$  in  $S_nS^{2-}$ , can be obtained from the difference in titrant volume between the third and second endpoints ( $S^{2-}$  in  $S_nS^{2-} = C-B$ ), whereas the carbonate concentration can be calculated from the volume difference between the fourth and third endpoints ( $Na_2CO_3 = D-C$ ). In highly oxidized liquors, a fifth endpoint (E), corresponding to the neutralization of 1 mol of  $Na_2S_2O_3$  per mole of acid [21], can generally be observed at a pH of 3 [ $Na_2S_2O_3 = 2(E-D)$ ]. However, the estimated thiosulphate concentration is not very accurate owing to the poor definition of the endpoint and to the potential contribution of formate ions to the endpoint volume (Eq. 16).

### Alkali Changes During Oxidation

If the reactions during oxidation of white liquor were correctly represented by Reactions 6 to 10, then the changes in alkali concentration before and after oxidation should provide some insights into the formation of polysulphide, thiosulphate, sulphite and sulphate ions. As mentioned previously, if the only species being formed were polysulphide ions of  $\bar{n} > 1$ , then  $OH^-$  ions would be produced (Reaction 6) and the EA concentration should increase. The gain in EA would depend not only on the amount of polysulphide generated but also on the mean chain length,  $\bar{n}$ , of polysulphide ions formed. Despite a higher EA, the AA should remain constant because the increase in  $OH^-$  concentration would be accompanied by a corresponding loss of titratable  $HS^-$  ions. In turn, if the oxidation reaction produced thiosulphate ions only (by Reactions 6 and 7 or by Reaction 8), then the EA should not change. However, because  $HS^-$  ions are con-

verted into a species ( $S_2O_3^{2-}$ ) non-titratable in the pH range where AA is determined, an increase in thiosulphate concentration of 1 g/L as  $Na_2O$  (or 1.032 g/L as S) should result in a drop of 1 g/L as  $Na_2O$  in the AA concentration. With polysulphides and thiosulphate both produced simultaneously, the EA concentration in the oxidized liquor should be higher but the AA should be lower. The concurrent production of sulphate ions by oxidation of hydrosulphide ions would complicate the alkali balance because an increase of 1 g/L, as  $Na_2O$ , of sulphate concentration would result in a loss of 0.5 g/L of EA and 1 g/L of AA.

To verify that, during oxidation, alkali changes with the stoichiometry of Reactions 6 to 10, literature data were first analyzed. Table II shows the variation in liquor composition when kraft white liquors from various sources were oxidized with air in the presence of a carbon catalyst to produce oxidized white liquors (OWL). In all cases, the EA increases with the formation of polysulphides. This evidence suggests that the  $\bar{n}$  value must be larger than one. Indeed, the  $\bar{n}$  values estimated from the literature data in Table II lie between 2.8 and 5.0. Although small variations in  $\bar{n}$  are to be expected because the liquors have different compositions, the range reported appears to be too large. According to Giggenbach [11],  $\bar{n}$  reaches a limiting value of 3.77 at 25°C. Thus the  $\bar{n}$  value of 5.0 in particular appears unreasonably high, although it is not surprising considering that  $\bar{n}$  values are calculated from the ratio between differences in EA and in polysulphide sulphur (PS) concentrations. It is also likely that the PS concentration in the four initial kraft liquors is not zero, as reported by the various groups. Based on many measurements, we have constantly found that PS concentrations ranged from 0.3 to 0.8 g of S/L in mill white liquors. In some instances, a concentration as high as 2.0 g/L was measured in unoxidized liquors. Thus,  $\Delta PS$  for a given  $\Delta EA$  may be over estimated in the examples presented in Table II. Based on the literature data, the increase

Alkali changes were less predictable, however, when oxidation was carried out in a pressurized pipeline reactor. Oxidation was carried out by injecting oxygen and/or air at four separate points along the reactor and cooled liquor samples could be taken before and after each gas sparger. The initial liquor temperature ranged between 85 and 95°C whereas the liquor temperatures rose to 105–150°C depending on the degree of oxidation. Analyses of liquor samples in most runs were limited to an acidimetric titration and to a polysulphide determination by gravimetry. However, samples from

[illegible][illegible]



some runs were also analyzed for sulphide and thiosulphate by  $\text{HgCl}_2$  titration and for sulphate and sulphite by ion chromatography. Unfortunately, results of sulphite analyses by ion chromatography were not only irreproducible but the values were far too high to be reasonable. Some of the problems associated with the analyses of sulphite ions in dilute kraft liquors by ion chromatography have been discussed by Donek et al. [17]. Thus the sulphite analyses are not reported here, although it is believed that proper determination of this ion would help to explain some of our poor sulphur balances.

Table IV shows representative results obtained during three pilot plant trials in the pipeline reactor. When the reactor was operated at relatively low pressure with a mixture of air and oxygen (run P1), the liquor temperature reached a maximum of 108°C. The chemical analyses show the characteristic increase of EA as polysulphide ions were formed, a loss of AA that can be explained by the formation of thiosulphate ions and no apparent increase in sulphate concentration during oxidation. At least under these mild operating conditions, changes in liquor compositions are similar to those produced during oxidation at atmospheric pressure (Tables II and III). For runs P2 and P3, the reactor was operated with a high oxygen flow rate (no air) under a pressure of 970 kPa; liquor temperatures reached 150°C at the outlet of the reactor. It was shown previously that, with this type of sample (OWL<sub>p</sub> in Tables II and III of Ref. [1]), polysulphide determination by gravimetry was affected by the degree of liquor dilution during acidification. The polysulphide determinations were thus determined with a lower sample size. As shown in Table IV, oxidation under pressure results in a slight decrease in PS concentration and in a drop of 3.0–3.8 g/L in EA concentration. Since the formation of sulphate ions combined with the small loss of polysulphide ions by oxidation can account for a maximum loss of 1 g/L of EA concentration, there must be another reaction responsible for the remaining loss of OH<sup>-</sup> ions. This reaction could take place during the EA determination by acidimetric titration or during oxidation.

It is clear, from Reaction 9, that the formation of sulphite ions is one pathway for alkali reduction. It is also possible that species other than polysulphide, thiosulphate, sulphite and sulphate are formed during oxidation. According to Gupta [24], trithionate ions ( $\text{S}_3\text{O}_6^{2-}$ ) are major products of weak black liquor oxidation. The stoichiometry involving polythionate formation does not however lead to the consumption of OH<sup>-</sup> unless the trithionate hydrolyzes to sulphate and thiosulphate ions. However, the small increase in sulphate concentration appears to rule out this reaction path. It is clear, from the rather poor sulphur balance and the unaccounted loss of EA, that more extended analyses will be required to fully explain our observations.

## CONCLUSIONS

Potentiometric curves of oxidized liquors produced by a titration with HCl using the standard ABC procedure exhibited more endpoints than a normal white liquor. Reactions between polysulphides, thiosulphate and formaldehyde were shown to be responsible for the appearance of new endpoints. Changes in alkali concentration as oxidation reactions proceeded were also shown to provide information on the formation of polysulphide, thiosulphate and sulphate ions.

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